

12 EUROPEAN PATENT APPLICATION

21 Application number: 84307757.9

51 Int. Cl.: C 01 C 1/04
C 01 B 3/02

22 Date of filing: 09.11.84

30 Priority: 10.11.83 US 550553

43 Date of publication of application:
19.06.85 Bulletin 85/25

84 Designated Contracting States:
FR GB NL

71 Applicant: Exxon Research and Engineering Company
P.O.Box 390 180 Park Avenue
Florham Park New Jersey 07932(US)

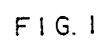
72 Inventor: Osman, Robert Michael
14 Stafford Road
Parsippany New Jersey(US)

72 Inventor: Byington, Robert George
38 Stone Run Road
Bedminster New Jersey(US)

74 Representative: Bawden, Peter Charles et al,
ESSO CHEMICAL LIMITED Esso Chemical Research
Centre PO Box 1
Abingdon Oxfordshire OX13 6BB(GB)

54 Improved low severity hydrocarbon steam reforming process.

57 In a process for producing ammonia which comprises: primary (4) and secondary (60) catalytically reforming shift conversion (80 and 90); carbon oxides removal (115); and ammonia synthesis (110), wherein at least a portion of an ammonia-depleted gas stream is recycled to the synthesis zone (110); and sidestream (134) of the ammonia-depleted gas is treated to separate a stream (142) enriched in hydrogen for return to the ammonia synthesis zone; the improvement which comprises: (i) operating step (b) at a temperature in the outlet gas of not greater than about 946°C and with an amount of air sufficient to provide from about 3 to 11 molar % excess N₂ and to form a secondary reformer outlet gas containing at least 0.8% vol. % methane; (ii) operating step (e) under conditions sufficient to provide at least 10 vol. % inert gases in the ammonia-depleted gas stream; and (iii) introducing as synthesis gas feed to the ammonia synthesis zone a mixture comprising the synthesis gas formed in step (d) having a methane content of at least about 1.2 mol.% CH₄, on a dry basis, the recycled gas produced in step (f) plus the hydrogen-enriched gas stream formed in step (g), whereby the H₂ loss from the process with the separated inerts enriched gas stream is minimized.



IMPROVED LOW SEVERITY HYDROCARBON STEAM REFORMING PROCESS

FIELD OF THE INVENTION

The present invention is directed generally to an improved process for the steam reforming of hydrocarbon gas feeds, and specifically to an improved low severity steam reforming process.

DESCRIPTION OF THE PRIOR ART

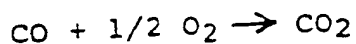
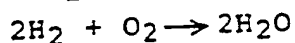
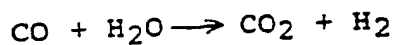
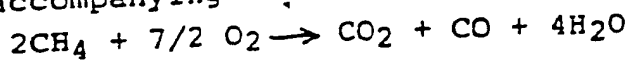
Generally, the manufacture of ammonia consists of preparing an ammonia synthesis gas from a nitrogen source, usually air, and from a hydrogen source, which is conventionally either coal, petroleum fractions, or natural gases. For example, in the preparation of ammonia synthesis gas from a light hydrocarbon feedstock, which may range from natural gas to naphtha, the hydrocarbon feedstock gas is first purified by removing gaseous contaminants, such as sulfur (which would poison the downstream catalysts) from the feedstock by the catalytic hydrogenation of the sulfur compounds to hydrogen sulfide and adsorption of the hydrogen sulfide over a zinc oxide adsorption medium. Subsequent steam reforming of the contaminant-free gas provides the major portion of the hydrogen required for ammonia synthesis from the hydrocarbons in the gas. Reforming is accomplished by a two-stage process in which a mixture of steam and the purified feed gas are first reformed over catalyst in a primary reformer, followed by treatment of the partially reformed gas in a secondary reformer to which air is introduced, in order to provide the required amount of N₂ for ammonia synthesis. A reformed gas is produced in the secondary reformer having a greater amount of hydrogen and a lesser amount of hydrocarbons. The reaction processes occurring in the reforming of the feedstock gas begin with the breakdown of hydrocarbons to methane, carbon dioxide and carbon monoxide:



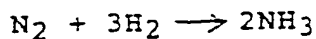
and end with the reforming of these products by the desired endothermic methane reforming reaction:



1 and by accompanying exothermic reactions:



6 The carbon monoxide in the reformed gas is con-
7 verted to carbon dioxide and additional hydrogen in one or
8 more shift conversion vessels, and the carbon dioxide is
9 removed by scrubbing. Further treatment of the raw synthe-
10 sis gas by methanation may be used to remove additional
11 carbon dioxide and carbon monoxide from the hydrogen-rich
12 gas, resulting subsequently in an ammonia synthesis gas
13 containing approximately three parts of hydrogen and one
14 part of nitrogen, that is, the 3:1 stoichiometric ratio of
15 hydrogen to nitrogen in ammonia, plus small amounts of
16 inerts such as methane, argon and helium. The ammonia
17 synthesis gas is then converted to ammonia by passing the
18 gas over a catalytic surface based upon metallic iron (con-
19 ventionally magnetite) which has been promoted with other
20 metallic oxides, and allowing the ammonia to be synthe-
21 sized according to the following exothermic reaction:



23 The effluent from the ammonia reactor, which
24 contains ammonia, unconverted H_2 and N_2 , and gases which
25 are essentially inerts in the ammonia reaction (princi-
26 pally, methane and argon), is then treated for ammonia
27 recovery, and to form a recycle stream containing H_2 and
28 N_2 which can be returned to the ammonia reactor along with
29 fresh ammonia synthesis gas.

30 In a conventional steam reforming ammonia pro-
31 cess, it is desirable to minimize the amount of unconvert-
32 ed hydrocarbons (methane slippage) leaving the reformers.
33 Methane will concentrate in the feed to the ammonia reac-
34 tors because H_2 and N_2 react and are removed as ammonia
35 product, but the major portion of the inerts such as meth-
36 ane is recycled along with the H_2 and N_2 and remains in
37 the reactor/recycle loop. If inerts buildup were left
38 unchecked, the partial pressure of the reactants (hydrogen

1 and nitrogen) would be reduced to the point where the re-
2 action rate would be uneconomically slow. To prevent this
3 excessive buildup, an inerts purge is generally taken,
4 conventionally going to fuel. Unfortunately, valuable
5 hydrogen (and nitrogen) is lost in the purge, which typ-
6 ically contains only 10-20% inerts. Minimizing reformer
7 methane slippage minimizes this loss, at the expense of
8 higher reformer furnace fuel and investment requirements.
9 Balances among these factors lead to conventional designs
10 having 7-12 dry mole % methane in the primary reformer
11 effluent.

12 Recent years have seen the development of var-
13 ious schemes for recovering most of the hydrogen from the
14 inerts purge stream. These purge recovery units have been
15 based on cryogenic fractionation, pressure swing adsorption
16 or membrane diffusion. What they all have in common is
17 that they produce two streams: one enriched in hydrogen
18 for recycle back to the ammonia reactor, and one enriched
19 in inerts going to fuel. An alternative approach to mini-
20 mizing purge hydrogen loss is the Kellogg purge converter
21 scheme, which employs a second ammonia synthesis reactor
22 to recover part of the purge gas hydrogen and nitrogen as
23 ammonia product. Regardless of which approach is used, a
24 purge gas hydrogen recovery unit saves energy by increasing
25 the conversion of feed to product by minimizing the amount
26 of valuable hydrogen downgraded to fuel. In a high energy
27 cost environment, the investment for a purge recovery unit
28 has often been justified on this basis, without signifi-
29 cant change to the operating conditions in the reforming
30 section of the plant.

31 U.S. Patent 3,081,268 (1963) employs an ex-
32 ternally fired primary reformer with high excess steam
33 (steam to feed gas carbon mole ratio of 4 to 8) to achieve
34 an exit gas having a temperature of from about 732°C to
35 899°C and a pressure of from about 345-1379KPa to achieve
36 conversion of 65 to 85% of the feed hydrocarbons to H₂ and
37 carbon oxides. This hydrocarbon conversion level is in-

1 creased further to 95%-99% overall, in a secondary reformer.
2 The secondary reformer effluent is treated in a shift con-
4 verter for CO removal, cooled and purified to form the
5 synthesis gas to the ammonia reactor.

6 U.S. Patent 3,442,613 (1969) to C. F. Braun &
7 Company disclose a process wherein excess methane and argon
8 present in the methanator effluent, are removed ahead of the
9 ammonia synthesis reaction zone by cryogenic techniques to
10 form a high purity synthesis gas and to allow minimization of
11 ammonia synthesis loop purge requirements. Related to the
12 Braun patent are B. J. Grotz, Hydrocarbon Processing, vol.
13 46, no. 4, pp. 197-202 (April 1967) and B. J. Grotz,
14 Nitrogen, vol. 100, pp. 71-75 (1976), and U.K. Patents
15 1,156,002 and 1,156,003.

16 In U.S. Patent 3,441,393 (1969) a Pullman process
17 is disclosed wherein the reforming, shift conversion and
18 methanation steps are accomplished such as to form an ammonia
19 synthesis gas and an ammonia reactor effluent gas dilute in
20 NH_3 (about 9.7% NH_3). A purge gas stream must be taken to
21 avoid inerts build-up, and the inerts level in the recycle
22 stream to the reactor is such that the combined (recycle and
23 fresh syn gas) feed to the reactor has from about 5 to 20
24 mol.% inerts.

25 U.S. Patent 3,947,551 (1976) to the Benfield Cor-
26 poration relates to a process in which the primary and sec-
27 ondary reforming conditions are such that a low methane con-
28 centration (about 0.3% CH_4) is present in the secondary re-
29 former effluent. Following shift conversion, CO_2 removal and
30 methanation, the ammonia synthesis gas is combined with a
31 recycle gas and passed to ammonia synthesis. Published U.K.
32 Patent Application 2,017,071A (1979) to Monsanto forms NH_3
33 from an ammonia synthesis gas containing from 2-15 vol.%
34 CH_4 , and $\text{H}_2:\text{N}_2$ mole ratios of from 2:1 to 4:1, to form a
35 reactor product gas containing from 10-25% NH_3 .

36 U.S. Patent 4,298,588 (1981) to ICI relates to a
37 process wherein primary reforming is accomplished with total

1 steam to carbon ratio of 2.5 to 3.5:1 to form an exit gas
2 (750-850°C, 30-120 bar) containing at least 10% and not more
3 than 30% CH₄, followed by secondary reforming with excess air
4 (above stoichiometric) to provide an effluent gas (950-
5 1050°C, about 30-120 bar) having from 0.2-10% CH₄ and a H₂:N₂
6 mole ratio of from 2.0 to 2.9:1. After shift conversion, CO₂
7 removal and methanation, the resulting fresh synthesis gas
8 (said to contain usually under 1% v/v of methane) is combined
9 with a H₂-rich recycle gas stream (at a ratio of recycled gas
10 to fresh gas of 4 to 6) and passed to an ammonia reactor to
11 give an ammonia reactor effluent gas containing 8 to 12 v/v%
12 NH₃. After removal of the ammonia product, the remaining gas
13 is partially recycled to the reactor and partially sent to a
14 purge recovery unit for removal of inerts and the excess N₂
15 (above stoichiometric) introduced with the fresh synthesis
16 gas. However, since H₂ recovery in conventional purge recov-
17 ery units is not complete, this process results in a high H₂
18 loss rate due to the need for a high flow rate of gases to be
19 treated in the purge recovery unit.

20 U.S. Patent 4,213,954 (1980) to ICI employs reform-
21 ing conditions and gas recycles similar to U.S. Patent
22 4,298,588.

23 Published European Application 49,967 (1982) to ICI
24 employs an adiabatic primary reforming step at lower primary
25 reformer outlet temperatures (<750°C, e.g., 550-650°C) than
26 those in the above discussed U.S. Patent 4,298,588. The
27 primary reformer effluent, containing 25 to 35% CH₄, is sub-
28 jected to secondary reforming with excess air at secondary
29 reformer outlet temperatures of <900°C, to form an outlet gas
30 containing from 1.5-3.0 mol.% CH₄ (dry basis) and a low H₂:N₂
31 ratio (1.0-2.5:1), and produce an ammonia reactor effluent
32 gas (after shift conversion, CO₂ removal and methanation)
33 having an ammonia content of about 14 mol.% which is passed
34 to ammonia recovery and thence partially to a purge gas re-
35 covery unit to form a H₂-rich recycle stream. Again, high H₂
36 losses result due to the need to treat a large volume of
37 gases in the purge recovery unit.

1 Illustrative purge recovery units are discussed in
2 U.K. Patents 1,057,020; 1,460,681 and 1,274,504; U.K. Patent
3 Application 2,030,473A; Russian Patent 486,667 (1973);
4 R. Banks, Chem. Eng., pp. 90-92 (October 10, 1977);
5 A. Haslam, et al., Hydrocarbon Processing, pp. 103-106
6 (January 1976); K. S. Chari, Chem. Age India, pp. 283-285
7 (April 1978), T. Matsuoka, Chem. Age India, vol. 30, no. 2,
8 pp. 119-128 (Feb. 1979); and R. L. Shaner, Chem Eng. Prog.,
9 pp. 47-52 (May 1978).

10 SUMMARY OF THE INVENTION

11 In a process for producing ammonia which comprises:
12 (a) primary catalytically reforming at super atmospheric
13 pressure in a direct-fired primary reforming zone, a
14 hydrocarbon feedstock with steam to produce a gas con-
15 taining carbon oxides, hydrogen and methane; (b) second-
16 dary catalytically reforming the gas from step (a) by
17 introducing air and bringing the mixture towards equili-
18 brium thereby producing a secondary reformer effluent gas
19 containing nitrogen, carbon oxides, hydrogen and a de-
20 creased quantity of methane; (c) converting carbon mon-
21 oxide catalytically with steam to carbon dioxide and
22 hydrogen; (d) removing carbon oxides to give an ammonia
23 synthesis gas comprising nitrogen and hydrogen and com-
24 pressing said gas to ammonia synthesis pressure; (e)
25 reacting the synthesis gas in an ammonia synthesis zone
26 to produce ammonia and recovering ammonia from the reac-
27 ted gas to produce an ammonia-depleted gas stream; (f)
28 recycling at least a portion of said ammonia-depleted gas
29 stream to said ammonia synthesis zone; and (g) treating a
30 sidestream of said ammonia-depleted gas to separate a
31 stream enriched in hydrogen and an inerts-enriched gas
32 stream, and returning the enriched hydrogen stream to the
33 ammonia synthesis zone; the improvement which comprises:
34 (i) operating step (b) at a temperature in the outlet gas
35 of not greater than about 946°C and with an amount of
36 air sufficient to provide from about 3 to 11 molar %
37 excess N₂, and to form a secondary reformer outlet gas

1 containing at least 0.8 vol.% methane; (ii) operating
2 step (e) under conditions sufficient to provide at least
3 10 vol.% inert gases in said ammonia-depleted gas stream;
4 and (iii) introducing as synthesis gas feed to the
5 ammonia synthesis zone a mixture comprising the synthesis
6 gas formed in step (d) having a methane content of at
7 least about 1.2 mol.% CH₄, on a dry basis, the recycled
8 gas produced in step (f) plus the hydrogen-enriched
9 gas stream formed in step (g), whereby the H₂ loss from
10 the process with the separated inerts enriched gas stream
11 is minimized.

12 BRIEF DESCRIPTION OF THE DRAWINGS

13 Figure 1 is a diagrammatic illustration of one
14 embodiment of the process of this invention.

15
16 DETAILED DESCRIPTION OF THE INVENTION

17 Referring to Figure 1, there is illustrated a di-
18 rect fired primary reforming furnace stage generally
19 indicated by the numeral 10, having convection section 4,
20 and primary reforming radiant section 18 heated by bur-
21 ners (not shown, and mounted, for example, in the floor
22 of the radiant section) which are supplied with fuel gas
23 14 and an oxidant gas (e.g., combustion air) 16 as illus-
24 trated. Hot flue gas exiting the radiant section flows
25 through convection section 4, past process steam super-
26 heat exchanger 21, process air (which may contain steam
27 and air) heat exchanger 26, power steam superheat ex-
28 changer 25, feed gas heat exchanger 24, and boiler feed
29 water preheater 22 and is discharged through stack 2.
30 Therefore, primary reformer 10 is direct fired by means
31 of the combustion of fuel gas 14 and the oxidant gas 16
32 therein. It will be understood that the direction of
33 flow of the hot combustion gases through primary reformer
34 10 is not critical, and primary reformer 10 can comprise
35 any conventional primary reformer design, such as is
36 illustrated in U.S. Patent 4,213,954, wherein the com-
37 bustion gas is passed downwardly from the upper portion

1 of the reformer's radiant section and wherein the convec-
2 tion section is horizontally disposed.

3 The two-stage reforming process requires the intro-
4 duction of four separate process streams to the primary
5 reformer: feed gas (for a source of hydrogen), steam, an
6 oxygen-containing gas and fuel gas. In addition, where
7 the process is intended for use in producing an ammonia
8 synthesis gas, a source of nitrogen gas (which is gen-
9 erally air) is generally added to the secondary reforming
10 stage.

11 Feed gas is introduced into the process via conduit
12 6 and passes through feed gas heat exchanger 24, posi-
13 tioned in the primary reforming furnace's convection
14 section 4. This preheats the feed gas to approximately
15 750°F. The gas feedstocks 6 which can be treated in ac-
16 cordance with the process of this invention can vary
17 widely. Suitable feed gases include coke gas or refinery
18 gases, such as are discussed in U.S. Patent 3,649,558, in
19 addition to coal pyrolysis gas, and feedstocks such as
20 those available from intermediate BTU gas (IBG) streams
21 resulting from the gasification of coal or lignite using
22 conventional gasification processes. Also suitable as
23 feeds are natural gas, naphtha, liquefied petroleum gas
24 (LPG), liquefied natural gas (LNG) and the like.

25 The heated feed gas is withdrawn from exchanger 24
26 via conduit 38, and may be admixed with a H₂ containing
27 gas 39 and contacted at elevated temperatures with a
28 conventional hydrodesulfurization catalyst such as a
29 supported Co-Mo or Ni-Mo hydrodesulfurization catalyst to
30 convert the S compounds in the feed gas to S forms which
31 can be removed in sulfur removal zone 44.

32 Alternatively, or in addition to hydrodesulfuriza-
33 tion zone 40, feed gas 38 can be admixed with sufficient
34 steam to supply the water of reaction required for a
35 subsequent COS hydrolysis reaction if COS is present in
36 the feed. The quantity of steam which is thus introduced
37 can vary widely and will generally comprise from about 2

1 to 4 vol.%, based on the total feed gas in conduit 38
2 withdrawn from exchanger 24. The COS reaction can be
3 effected by any conventional means, using conventional
4 hydrolysis catalysts such as activated alumina. In this
5 reactor, COS contained in the feed gas is converted into
6 hydrogen sulfide gas at conventional hydrolysis condi-
7 tions, which typically range from about 149 to 177°C and
8 from about 2069 to 4137 kPa.

9 The gas mixture resulting from the hydrodesulfur-
10 ization treatment (or from such a COS hydrolysis step)
11 may contain hydrogen sulfide, and is introduced via con-
12 duit 42 into sulfur removal zone 44, generally at a gas
13 temperature of from about 316 to 399°C wherein hydrogen
14 sulfide impurities are removed from the gas stream by
15 conventional technology, such as by use of a zinc oxide
16 adsorption bed. The gas, now essentially free of sulfur
17 impurities (e.g., containing less than about 0.2 ppm by
18 weight of sulfur compounds, calculated as elemental sul-
19 fur), is withdrawn via conduit 54 and admixed with steam,
20 which can be accomplished by injecting steam into conduit
21 54 via conduit 12 and which can comprise at least a por-
22 tion of steam turbine 50 exhaust. Normally, either the
23 turbine steam exhaust steam 12, is heated before mixing
24 with a desulfurized feedstock gas, or this exhaust steam
25 is first admixed with a feedstock gas and the resulting
26 mixture is heated, before being passed to the primary
27 reforming step. The quantity of steam introduced at this
28 point will generally range from about 2.5 to 5.0 moles of
29 steam per mole of carbon in the desulfurized gas feed.
30 The function of the steam introduced at this point in the
31 process is to provide the water of reaction necessary for
32 the subsequent reforming reactions. The steam/desulfur-
33 ized gas mixture is then introduced into the tubes 56 of
34 direct fired primary reformer 10 wherein the feed gas is
35 at least partially reformed by contacting the feed gas,
36 under reforming conditions, in tubes 56 with a conven-
37 tional reforming catalyst. Any conventional primary

1 reforming catalyst can be employed, such as nickel,
2 nickel oxide, chromia, molybdenum, mixtures thereof and
3 the like, with nickel-on-calcium aluminate or nickel-on-
4 alumina being preferred. The temperature within tubes
5 56 will generally range from about 427 to 816°C. and
6 preferably from about 538 to 788°C, and the pressure
7 will generally range from about 2069 to 6900 kPa, and
8 preferably from about 3100 to 4137 kPa, and the total gas
9 hourly space velocity in tubes 56 will generally range
10 from about 5000 to 15,000 v/v/hr., with a range of from
11 6000 to 10,000 v/v/hr. being preferred.

12 As a result of the reforming reactions occurring in
13 tubes 56 of primary reformer 10, substantially all of the
14 hydrocarbon components of the feed gas (other than meth-
15 ane) are converted to CH₄, CO, CO₂ and H₂; a portion of
16 the original methane component is likewise converted to
17 CO, CO₂ and H₂; and the temperature of the gas mixture
18 will be generally increased to about 677 to 802°C, and
19 preferably from about 732 to 788°C. According to the
20 process of this invention, the partially reformed gas 58
21 will have a residual methane level of at least 13 vol.%
22 CH₄, and preferably from about 15 to 20 vol.% CH₄, on a
23 dry basis.

24 The hot combustion gases travel past the exterior
25 of tubes 56 out of radiant section 18 and into convection
26 section 4 wherein the hot gases contact heat exchangers
27 21, 26, 25, 24, and 22, for recovery of heat by exchange
28 with various streams. The precise number and sequence of
29 the convection section heat exchangers can be chosen
30 using conventional techniques to minimize investment
31 and/or maximize energy recovery. (For example, one or
32 more of the illustrative heat exchangers may be split
33 into separate units in convection section 4 to achieve a
34 more favorable temperature profile.) Boiler feed water 8
35 is passed through heat exchanger 22 and withdrawn via
36 conduit 30 and can be passed to a steam drum (not shown)
37 from which steam can be withdrawn and passed for

1 superheating through heat exchange with one or more of
2 the secondary reformer effluent 62, high temperature
3 shift effluent 82 or ammonia reactor effluent 112, and
4 then preferably passed via conduit 20 for further super-
5 heating in convection section exchanger 25 to achieve a
6 steam temperature of approximately 482°C. This steam is
7 then passed via conduit 36 to turbine 50 to generate
8 work, and the resulting steam from turbine exhaust line
9 52 is partially withdrawn via conduit 28 and the re-
10 mainder is passed to heat exchanger 21 for reheating of
11 the exhaust steam to about 649°C in indirect heat
12 exchange in convection section 4, and thence to conduit
13 12. The thus reheated steam is combined with the
14 desulfurized feed gas and fed to catalyst-filled reformer
15 tubes 56 in radiant section 18. A particularly preferred
16 method of forming superheated steam 38 is described in
17 the copending application "Hydrocarbon Steam Reforming
18 Using Series Steam Superheaters", Attorney Docket No. CS-
19 307, filed herewith, the disclosure of which is hereby
20 incorporated by reference.

21 Process air obtained from any convenient source is
22 preheated by passing it to the primary reformer con-
23 vection section heat exchanger 26 wherein it is heated
24 (generally to a temperature of from about 482 to 704°C)
25 by indirect heat exchange with the hot primary reformer
26 convection gas. Prior to or at an intermediate point in
27 the heating process, the process air may be mixed with a
28 portion of turbine exhaust steam 13. The thus-heated
29 process air (with or without admixed steam) is introduced
30 via conduit 34 into secondary reformer 60, together with
31 the partially reformed gas mixture which is introduced
32 via conduit 58.

33 The quantity of air introduced via conduit 34 is
34 adjusted using conventional control means (not shown), to
35 provide an air:feed ratio sufficient to yield a hydro-
36 gen:nitrogen ratio in the methanator effluent gas 99, of
37 from about 2.7:1 to 2.9:1, that is from about 3 to 11

1 molar % excess N_2 . Generally the mole ratio in the
2 secondary reformer effluent gas 62 will range from about
3 2.0:1 to 2.8:1 $H_2:N_2$, and preferably from about 2.2:1 to
4 2.6:1 $H_2:N_2$.

5 Secondary reformer 60 can comprise an adiabatic re-
6 former of conventional design and during steady-state
7 operation achieves further reforming by means of the heat
8 released therein from the exothermic reaction of oxygen
9 with partially reformed feedstock. The amount and type
10 of catalyst in reformer 60 is also conventional, with Ni
11 catalysts supported on alumina being typical. In the
12 process of this invention, the secondary reformer outlet
13 temperature will be less than about $946^{\circ}C$. and prefer-
14 ably from about 882 to $938^{\circ}C$. the secondary reformer
15 outlet pressure will generally range from about 2069 to
16 6900 kPa and preferably from about 3100 to 4137 kPa, and
17 a total gas hourly space velocity of from about 6000 to
18 10,000 v/v/hr will be generally employed.

19 The secondary reformer effluent gas 62, generally
20 having a residual CH_4 level of at least about 0.8 vol.%
21 CH_4 , and preferably from at least about 1 vol.% up to
22 about 2 vol.% CH_4 (on a dry basis), is withdrawn from
23 secondary reformer 60 and passed to heat recovery zone
24 70, which can comprise a saturated high pressure steam
25 generator, steam superheat exchanger or a combination
26 of one or more such generators and steam superheaters.
27 The resulting partially cooled secondary reformer
28 effluent is withdrawn via conduit 72 and then passed to
29 high temperature shift converter 80, wherein carbon
30 monoxide in the reformer effluent gas is converted over
31 conventional catalysts and using conventional methods
32 and equipment to carbon dioxide and additional
33 hydrogen.

34 Generally, a temperature of from about 316 to
35 $482^{\circ}C$ and a pressure of from about 2069 to 6900 kPa
36 will be employed in shift converter 80, and the
37 catalyst will generally comprise a supported, chromium-

1 promoted iron catalyst. Thereafter, gas exiting the
2 high temperature shift converter is withdrawn via
3 conduit 82 and is passed to a heat recovery zone 84,
4 which can include a second steam generator. The
5 partially cooled high temperature shift effluent from
6 zone 84 is fed to low temperature shift converter 90,
7 or preferably first to guard bed 88.

8 Guard bed 88, which is optional, is preferably
9 employed to treat gas stream 86 upstream of low
10 temperature shift converter 90 to remove halide and
11 sulfur impurities and thereby protect any halide- and
12 sulfur-sensitive catalyst in low temperature shift
13 converter 90. The operation of guard bed 88 and the
14 type of catalyst used therein (e.g., zinc oxide
15 promoted with copper oxide), is conventional, and this
16 step is generally conducted at temperatures and
17 pressures within the ranges used in low temperature
18 shift converter 90 as described below, and the solids
19 employed in guard bed 88 for such halide- and S-
20 impurities removal can comprise the same catalyst as is
21 used in low temperature shift converter 90.

22 In shift converter 90, a low temperature shift
23 conversion reaction is effected over conventional cata-
24 lyst using conventional methods and equipment to form
25 additional quantities of H_2 and CO_2 . Generally, a tem-
26 perature of from about 204 to 260°C and a pressure of
27 from about 2069 to 6900 kPa will be employed in converter
28 90, and the catalyst will generally comprise a mixture of
29 zinc and copper oxides. The effluent gas from low tem-
30 perature shift converter 90 is then cooled in third heat
31 recovery zone 94 (which can comprise one or more heat
32 exchange vessels), and the cooled, low temperature shift
33 converter effluent gas, now depleted of its heat values,
34 is passed via conduit 113 to CO_2 -removal zone 115, in
35 which any conventional process (e.g., solvent absorption
36 of CO_2 gas) can be used to remove CO_2 via conduit 111.
37 The resulting, substantially CO_2 -free gas is fed by con-

1 duit 96 to conventional methanator zone 98 (which nor-
2 mally includes one or more heat exchangers) for removal
3 of additional CO and CO₂ and is then withdrawn (via con-
4 duit 99) and combined with H₂ enriched recycle stream 142
5 to form stream 101 which is compressed in compressor 100
6 to ammonia synthesis pressure. The methanator effluent
7 gas 99 in the process of this invention comprises the
8 fresh or "make-up" synthesis gas and is characterized by
9 a CH₄ concentration of at least about 1.2 vol.% (dry
10 basis), and preferably from about 1.4 to 2.2 vol.% CH₄
11 (dry basis), prior to the introduction of any recycle gas
12 stream 142.

13 The pressurized synthesis gas 102 is admixed with
14 recycle stream 132 and preheated in heating zone 104
15 (which can comprise an indirect heat exchanger in which
16 the hot ammonia reactor effluent gas, or a gas from one
17 or more catalyst stages thereof, is used as the heating
18 medium). The preheated feed gas is then passed via con-
19 duit 106 to ammonia reactor 110 wherein NH₃ is formed
20 from the generally stoichiometric H₂/N₂ in the synthesis
21 gas feed 106 (i.e., about 3:1 H₂:N₂ molar ratio) using
22 conventional techniques (i.e., over Fe-catalyst at 316 to
23 538°C). A gaseous ammonia reactor effluent is withdrawn
24 via conduit 112 and cooled in heat recovery zone 114
25 which can comprise heat exchangers, boilers, and the
26 like, and the cooled ammonia reactor effluent is passed
27 to ammonia recovery zone 120 wherein ammonia product 122
28 is recovered (e.g., by refrigeration to condense the
29 ammonia therein), thereby forming a gas stream 124
30 comprising unreacted N₂, H₂, residual NH₃ and inerts to
31 the ammonia reaction (e.g., CH₄, Ar, and He), which can
32 be heated in heating zone 126, passed via conduit 128 to
33 circulator 130 and recycled via conduit 132 to the
34 ammonia synthesis reactor feed upstream of feed preheater
35 104. If desired, the cool recycle gas 124 can be heated
36 by indirect exchange with ammonia reactor effluent gas
37 112, in which case heater 126 will comprise at least one
38 heat exchanger in heat recovery zone 114. Normally,

1 liquid ammonia stream 122 is flashed (i.e., depressured)
2 to remove dissolved gases (H_2 , CH_4 , N_2 , Ar and He) as a
3 flash gas, which can be passed to fuel use.

4 It is a feature of this invention that the recycle
5 gas stream 128 and hence recycle gas stream 132, contains
6 inerts (CH_4 , Ar, and He) in an amount of at least 10
7 vol.%, and preferably from about 12 to 20 vol.%, and will
8 generally contain H_2 and N_2 in a mol ratio of from about
9 2.5 to 3.5 $H_2:N_2$. The volume of recycle gas stream 132
10 will generally comprise from about 65 to 85 vol.% of the
11 total pressurized gas stream 106, and the recycle gas
12 (stream 132) to fresh feed (stream 102) mole ratio will
13 therefore be at least 2:1, and preferably from about 2.5
14 to 3.9:1. At least a portion, and generally from about
15 2.5 to 6 vol.% (and preferably from about 3 to 4.5
16 vol.%), of the warmed recycle gas 128 is withdrawn via
17 conduit 134 and passed to purge recovery zone 140 wherein
18 the gas is treated to separate an inerts purge stream 138
19 enriched in CH_4 and Ar (which can be used, if desired, as
20 a fuel gas) and to form an H_2 -enriched gas 142 which is
21 recycled to the ammonia reaction, e.g., by admixing with
22 methanator effluent 99 (which can be accomplished prior,
23 after or during compression in compressors 100). The
24 $H_2:N_2$ mole ratio in recycle stream 142 will generally
25 range from about 5 to 20:1, and preferably from about 7
26 to 15:1. The volume of the recycle stream 142 will
27 generally be from about 5 to 12 vol.% of the volume of
28 the fresh synthesis gas stream 99.

29 The manner of operation of CO_2 removal zone 115,
30 methanation zone 98, compressor 100 and NH_3 synthesis
31 zone 110 can be readily ascertained by one of ordinary
32 skill in the art to achieve the above-described objec-
33 tives, and need not be more completely described for a
34 full understanding of the process of this invention. The
35 precise operating parameters and equipment of each such
36 process step, therefore, will be readily apparent to one
37 having ordinary skill in the art, and each step can in-
38 clude the usual internal recycle streams and stages found

1 useful in the prior art. Thus, CO₂-removal zone 115 can
2 include conventional CO₂-absorption and CO₂ desorption
3 stages wherein the CO₂-laden gas 113 is contacted with a
4 liquid containing either a solvent for, or a dissolved
5 compound (e.g., K₂CO₃) readily reactive with, the CO₂;
6 the CO₂-free gases (generally containing less than about
7 0.3 vol.% CO₂) are withdrawn; and the solvent is treated
8 to desorb the CO₂ gases 111 for recycle of solvent to the
9 absorber. Zone 115 can also employ conventional pressure
10 swing adsorption methods for CO₂ removal. Exemplary of
11 suitable conventional CO₂ removal systems are those dis-
12 cussed in Kirk-Othmer, Encyclopedia of Chemical Tech-
13 nology, 3d ed., vol. 2, pp. 492-494 (1978). Similarly,
14 methanator 98 will generally employ a temperature in the
15 range of about 260 to 482°C, a pressure from about 2069 to
16 6900 kPa, and a supported Ni catalyst (e.g., Ni on alu-
17 mina) to convert any remaining CO and CO₂ in gas stream
18 96 to methane, thereby producing an effluent gas 99
19 containing less than about 10 vppm (i.e., parts per
20 million by volume) of total CO and CO₂ and H₂ and N₂ in
21 a H₂:N₂ molar ratio of from about 2.7:1 to 2.9:1. Com-
22 pression in zone 100 can take place in several stages,
23 as desired, to bring the methanator effluent to syn-
24 thesis reactor pressure, which generally ranges from
25 about 10,340 to 34,470 kPa. (If desired, compressors 100
26 can be located upstream of zone 115, to compress the
27 gas prior to treatment in zone 115.) Finally, a con-
28 ventional dryer unit (not shown) can be employed
29 wherein trace water is removed from the fresh syn gas
30 99 as required. (If desired, such conventional dryer
31 units can be located to treat stream 101 or at an
32 intermediate point within gas compression zone 100.)

33 A wide variety of processes can be employed in
34 zone 140 to treat gas stream 134 for removal of inerts
35 and excess N₂ (above stoichiometric) as purge via con-
36 duit 138. The operation of the purge recovery zone 140
37 can be easily ascertained by one skilled in the art and

1 forms no part of the present invention. Therefore,
2 suitable purge recovery processes include cryogenic
3 methods, wherein the gas stream 134 is cooled for re-
4 moval of inerts, such as methane and argon; pressure
5 swing adsorption; and membrane diffusion processes for
6 recovery of a hydrogen-enriched gas stream and separa-
7 tion of the inerts. Suitable are purge recovery pro-
8 cesses disclosed in U.K. Patents 1,057,020; 1,460,681
9 and 1,274,504; U.K. Patent Application 2,030,973A;
10 Russian Patent 486,667 (1973); R. Banks, Chem Eng, pp
11 90-92 (Oct. 10, 1977); A. Haslam et al., Hydrocarbon
12 Processing, pp 103-106 (January 1976); K. S. Chari,
13 Chem. Age India, p. 283-285 (April 1978); T. Matsuoka,
14 Chem. Age India, vol. 30, no. 2, pp. 119-128 (Feb.
15 1979); and R. L. Shaner, Chem. Eng. Prog, pp. 47-52
16 (May 1978).

17 The improved process of this invention produces a
18 syn gas 102, having a $H_2:N_2$ molar ratio of about 3:1,
19 that is a $H_2:N_2$ molar ratio of from about 2.6:1 to
20 3.2:1, and a residual methane concentration (dry basis)
21 of from about 1 to 3 vol.%, and more preferably from
22 about 1.2 to 2.2 vol.%, and which is therefore particu-
23 larly suitable, after combination with recycle gas
24 stream 132 (to form a combined syn gas reactor feed
25 stream 106 containing preferably from about 7 to 13
26 vol.% CH_4 , dry basis), for direct feed to an ammonia
27 synthesis reactor zone 110. Therefore, it is not
28 necessary in the process of this invention to treat gas
29 streams 99, 101 or 102 in a cryogenic purification step
30 to remove excess methane and N_2 prior to the ammonia
31 synthesis reaction. (However, if desired, syn gas 101
32 can be subjected to a cryogenic purification prior to
33 introduction into ammonia synthesis reactor zone 110,
34 for example by use of the cryogenic purification method
35 of U.S. Patent 3,442,613, the disclosure of which is
36 hereby incorporated by reference.)

1 The improved process of this invention can be
2 further illustrated by reference to the following exam-
ples.

3 EXAMPLE 1

4 Referring to the process of this invention, as
5 illustrated in Fig. 1, the process is employed to pro-
6 duce 1000 metric tons/day of ammonia using the feed-
7 stream and process conditions summarized in Table 1.

8 The conditions of Example 1 were derived using
9 the following bases, typical of those which would be
10 used in designs of commercial ammonia manufacturing
11 plants: a leak loss allowance of 1 mol.% of gas flow
12 through synthesis gas compressor 100, 29 kgmmole/hr of
13 desulfurization hydrogen (stream 39) comprising a side-
14 stream (not shown) taken from the H₂-enriched recycle
15 stream 142, and 14.5 kgm mole/hr of hydrogen and 7 kgm
16 mole/hr of ammonia in the flash gas going to fuel.
17 (The flash gas is the gas evolved when the liquid am-
18 monia 122, condensed out from ammonia synthesis reactor
19 effluent 116, is depressured to evolve any H₂, N₂, CH₄,
20 Ar and He dissolved therein.) Also, purge hydrogen
21 recovery unit 140 is of a cryogenic type having the
22 following net recoveries of the various feed components
23 (net component recovery is defined as the percentage of
24 a given component in purge 134 recovered in stream
25 142):

26	H ₂	87.64 mol. %
27	N ₂	25.61
28	CH ₄	3.66
29	Ar	15.70
30	He	99.00

31 It should be noted that these net recoveries
32 include a leak loss allowance of 1 mol.% of the purge
33 gas fed to unit 140.

TABLE 1

	Primary Reformer Feed (Stream 54 + 12)	Primary Reformer Effluent (Stream 58)	Air + Steam to Secondary Reformer (Stream 34)	Secondary Reformer Effluent (Stream 62)	Final Synthesis Gas (Stream 99)
1					
2					
3					
4					
5					
6					
7	Wet flowrate, mph	5180.5	2339.8	9516.5	5280.0
8	Pressure, kPa	3792.0	3448.0	3406.0	2882.0
9	Temperature, °C	562.8	773.9	921.5	4.4
10	Composition, drymol. %				
11	CH ₄	91.98	16.38	1.05	1.73
12	C ₂ H ₆	2.35	-	-	-
13	C ₃ H ₈	1.13	-	-	-
14	C ₄ H ₁₀	0.49	-	-	-
15	N ₂	1.73	78.09	23.03	25.67
16	CO ₂	0.34	0.03	8.77	-
17	H ₂	1.93	-	55.58	72.29
18	Ar	0.01	0.93	0.27	0.30
19	O ₂	-	20.95	-	-
20	CO	-	-	11.29	-
21	He	0.04	0.01	0.01	0.01
22	Steam/Dry Gas Ratio	3.264	0.820	0.614	0.0008

COMPARATIVE EXAMPLES 2 AND 3

Again, referring to the process illustrated in Figure 1, a series of cases are exemplified in Table 2, in which a comparison is given between the process of this invention as illustrated in Figure 1, and Comparative Examples 2 and 3, which progressively illustrate the adverse effects of moving away from this invention by using additional air introduction to the secondary reformer as a means to raise secondary reformer outlet temperature above 946°C, while correspondingly reducing methanator effluent methane content. Purge recovery unit component recovery fractions were assumed to be the same for each case, as were compressor leak loss, flash gas to fuel and desulfurization hydrogen requirement.

Looking first to Comparative Example 2, Table 2 indicates that an increase in secondary reformer outlet temperature to 950°C (vs. 921.5°C in Example 1) can be achieved via an increase in dry process air flow rate of 9.1% (from 1712 kgm mole/hr to 1868 kgm mole/hr). This also causes the secondary reformer effluent methane content to drop from 1.05% to 0.63% (dry molar basis), and the methanator effluent methane content to drop from 1.78% to 1.26% (dry molar basis). Due to the extra nitrogen being introduced with the additional air, the methanator effluent H₂/N₂ ratio drops from 2.82 to 2.60.

The greater degree of feed methane conversion in Comparative Example 2 (i.e., the lower secondary reformer effluent methane content) leads to an increase in the methanator effluent H₂ flow of 0.7% (from 3814 kgmmole/hr to 3841 kgm mole/hr). However, this apparent advantage for Comparative Example 2 over Example 1 is misleading, because the lower methanator H₂/N₂ ratio requires that the ammonia synthesis zone employ a substantially higher purge rate to bring the ratio up to

the vicinity of the stoichiometric value of 3.0 at the inlet to the ammonia synthesis reactor 110. The higher purge rate in turn substantially increases the loss of H_2 to fuel (in stream 138) due to imperfect H_2 recovery in purge H_2 recovery unit 140. The net effect is that, despite the higher methanator effluent H_2 , the H_2 actually converted to ammonia is lower (3631 kgm mole/hr) for Comparative Example 2 than for Example 1 (3675 kgm mole/hr). Thus, after accounting for ammonia lost in the flash gas going to fuel, Comparative Example 2 only produces 988 MeT/SD of net ammonia product vs. 1000 MeT/SD for Example 1 with the same feed rate and reformer furnace firing.

Specifically, Example 2 uses a higher purge rate of 1388 kgmmole/hr vs. 684 kgm mole/hr for Example 1 (ammonia-free basis), so that the purge recovery unit product stream 142, containing a high percentage of H_2 , can blend with stream 99 to achieve a 3.0 H_2/N_2 ratio in stream 101 in each Example. A manifestation of the higher purge rate is the greatly reduced inerts content in the purge stream. As indicated in Table 2, the Comparative Example 2 purge contains only 6.6% inerts, vs. a more conventional 15.9% for Example 1 (both values on ammonia-free basis). Thus, it is shown that very low purge inerts contents (i.e., less than 10%) are characteristic of high H_2 losses to fuel.

Looking next at Comparative Example 3, Table 2 indicates that a further increase in secondary reformer outlet temperature to 1000°C can be achieved via an additional 15.4% increase in process air flow rate (to 2132kgm mole/hr); that is a total of 24.5% increase in process air flow rate as compared to Example 1. With this further air rate increase, the secondary reformer effluent methane content drops down to 0.23% (dry molar basis) and the methanator effluent methane content falls to 0.80 dry mole %. The corresponding methanator effluent H_2/N_2 ratio is only 2.29.

1 Comparative Example 3 yields a slight further
2 increase in the H₂ flow rate leaving the methanator of
3 0.2% (to 3849kgm mole/hr). However, as with Compara-
4 tive Example 2, the net effect is negative, with H₂
5 actually converted to ammonia dropping to only 7736 lb
6 mole/hr, and net ammonia production falling to 955
7 MeT/SD. Characteristic of the low methanator effluent
8 H₂/N₂ ratio and the low net H₂ conversion to ammonia,
9 the purge rate is high (2678kgm mole/hr on ammonia-free
10 basis), and purge inerts content is low (2.8% on am-
11 monia-free basis).

12 In addition, the higher process air flow rates of
13 Comparative Examples 2 and 3 result in an increased
14 consumption of energy in compression of the air, a
15 significant process cost for an ammonia plant.

TABLE 2

Process Parameter	Stream NO.	Example 1	Comparative Example 2	Comparative Example 3
Primary Reformer				
Inlet Steam/Carbon (1)	54 + 12	3.2	3.2	3.2
Outlet Temperature, °C	58	774	774	774
Outlet Pressure, kPa	58	3792	3792	3792
Outlet CH ₄ Slip, dry mole %	58	16.4	16.4	16.4
Secondary Reformer (8)				
Dry Air Rate kgm mole/hr	34	1712	1868	2132
Excess Air, mole % (2)	34	6.5	15.3	31.1
Steam/Dry Air Mole Ratio	34	0.367	0.336 (5)	0.294 (5)
Outlet Temperature, °C	62	922	950	1000
Outlet Pressure, kPa	62	3406	3406	3406
Outlet CH ₄ Slip dry mole %	62	1.05	0.63	0.23
Methanator Effluent				
H ₂ Flow, kgm mole/hr	99	3814	3841	3849
H ₂ /N ₂ mole ratio	99	2.82	2.60	2.29
Outlet CH ₄ Content, dry mole %	99	1.78	1.26	0.80
Ammonia Synthesis Loop				
Purge rate, kgm mole/hr (3)	134	684	1388	2678
Purge inerts content, mole % (3)	134	15.9	6.6	2.8
Unconverted H ₂ , kgm mole/hr	(4)	139	210	340
H ₂ converted to NH ₃ , kgm mole/hr	110	3675	3631	3509
NH ₃ in flash gas to fuel, kgm mole/hr	(6)	3.2	3.2	3.2
Net NH ₃ Production, MeT/SD	(7)	1000	988	955

See footnotes next page

TABLE 2

FOOTNOTES CONTINUEDNotes:

- (1) Ratio of moles of steam to moles of hydrocarbon carbon (excludes CO₂) in feed gas.
- (2) Air in excess of that required to produce a stoichiometric 3.0 H₂/N₂ mole ratio in the methanator effluent stream.
- (3) Purge rate and purge inerts % are reported on an ammonia-free basis. Inerts are CH₄, Ar and He.
- (4) Includes synthesis compressor 100 leak loss allowance, desulfurization H₂ 39, flash gas H₂, purge recovery unit fuel gas product 138 and purge recovery unit leak loss allowance.
- (5) Flow of steam in stream 34 held constant at same rate as in Example 1.
- (6) Assumes stream 122 is depressured to remove inerts as flash gas.
- (7) Ammonia in liquid product stream after flash of stream 122 for removal of inerts.
- (8) The temperature of the air/steam mixture 34 going to the secondary reformer was held constant at 649°C.

Thus, while I have illustrated and described the preferred embodiment of my invention, and have described my invention and the manner and process of making and using it in such full, clear, concise and exact terms as to enable any person skilled in the art to which it pertains to make and use the same, one skilled in the art can easily ascertain the essential characteristics of this invention and without departure from the spirit and scope thereof can make various changes and/or modifications to the invention for adapting it to various usages and conditions. Accordingly, such changes and/or modifications are properly intended to be within the full range of equivalents of the following claims.

All pressures mentioned herein are in units of kilopascals gauge.

WHAT IS CLAIMED IS:

1. In a process for producing ammonia which comprises:

- (a) primary catalytically reforming at super atmospheric pressure in a direct-fired primary reforming zone, a hydrocarbon feedstock with steam to produce a gas containing carbon oxides, hydrogen and methane;
- (b) secondary catalytically reforming the gas from step (a) by introducing air and bringing the mixture towards equilibrium thereby producing a secondary reformer effluent gas containing nitrogen, carbon oxides, hydrogen and a decreased quantity of methane;
- (c) converting carbon monoxide catalytically with steam to carbon dioxide and hydrogen;
- (d) removing carbon oxides to give an ammonia synthesis gas comprising nitrogen and hydrogen and compressing said gas to ammonia synthesis pressure;
- (e) reacting the synthesis gas in an ammonia synthesis zone to produce ammonia and recovering ammonia from the reacted gas to produce an ammonia-depleted gas stream;
- (f) recycling at least a portion of said ammonia-depleted gas stream to said ammonia synthesis zone; and
- (g) treating a sidestream of said ammonia-depleted gas to separate a stream enriched in hydrogen and an inerts-enriched gas stream, and returning the enriched hydrogen stream to the ammonia synthesis zone;

the improvement which comprises:

- (i) operating step (b) at a temperature in the outlet gas of not greater than about 946°C and with an

amount of air sufficient to provide from about 3 to 11 molar % excess N_2 , and to form a secondary reformer outlet gas containing at least 0.8 vol.% methane;

- (ii) operating step (e) under conditions sufficient to provide at least 10 volume percent inert gases in said ammonia-depleted gas stream; and
- (iii) introducing as synthesis gas feed to the ammonia synthesis zone a mixture comprising the synthesis gas formed in step (d) having a methane content of at least about 1.2 mole % CH_4 , on a dry basis, the recycled gas produced in step (f) plus the hydrogen-enriched gas stream formed in step (g), whereby the H_2 loss from the process with the separated inerts-enriched gas stream is minimized.

2. The improved process of claim 1 wherein step (b) is operated at a temperature in the outlet gas of from about 882 to 938°C.

3. The improved process of claim 2 wherein step (b) is operated at an outlet gas pressure of from about 2758 to 4137 kPa and wherein the outlet gas of step (b) contains from about 1 to 2 volume percent methane, on a dry basis.

4. The improved process of claim 1 wherein from about 2.5 to 6 volume percent of said ammonia-depleted gas is passed as said sidestream to step (g).

5. The improved process of claim 4 wherein said ammonia-depleted gas stream contains from about 10 to 20 volume percent inerts.

6. The improved process of claim 5 wherein said synthesis gas feed to the ammonia synthesis zone contains from about 7 to 13 volume percent methane.

7. The improved process of claim 1 wherein said ammonia-depleted gas stream contains from about 10 to 20 percent inerts and is characterized by a hydrogen:nitrogen mole ratio of from 2.5 to 3.5:1.

8. The improved process of claim 1 wherein step (a) is operated at an outlet gas temperature of from about 677 to 802°C, at a steam to carbon molar ratio of from 2.5 to 5.0:1 and employs an outlet gas methane content of at least about 13 volume percent, on a dry basis.

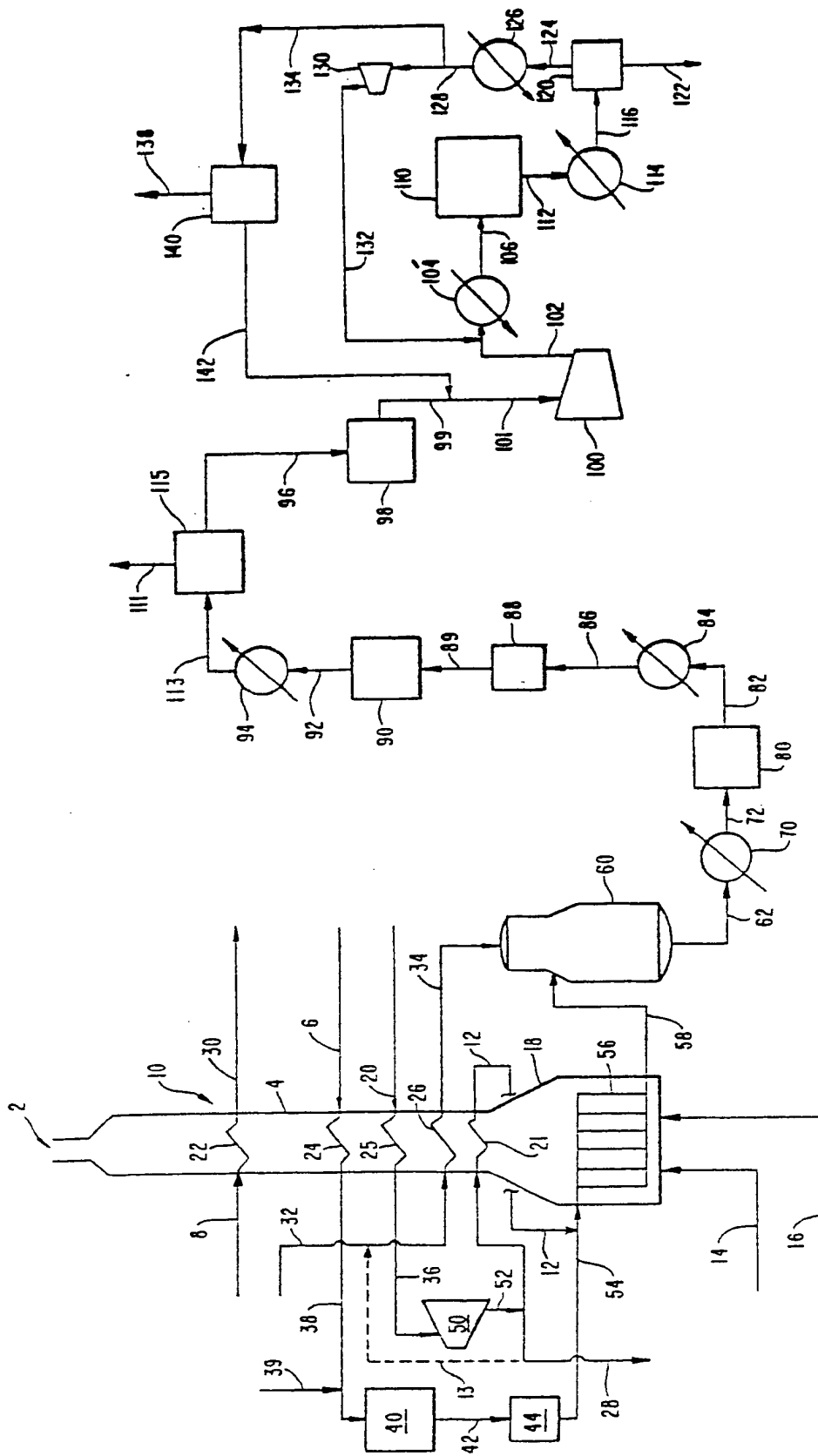


FIG. 1